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(54) Title: Aqueous Fluorocopolymer Dispersion [English]

(54) Title of the Invention: An Aqueous Fluorocopolymer Dispersion [Japanese]

(57) Abstract [Japanese]

[The invention] is an aqueous fluorocopolymer dispersion prepared by the seed polymerization of 20 to 100 parts by weight of an acrylic acid ester and/or methacrylic acid ester in an aqueous dispersion containing fluorocopolymer particles comprised of 70 to 95 mole % of vinylidene fluoride and 5 to 30 mole % of chlorotrifluoroethylene in the presence of 100 parts by weight of said fluorocopolymer particles. It is of superior film forming capacity, transparency in clear coating and weathering resistance and can provide a coating film having a high gloss and superior mechanical properties.

SPECIFICATION

An Aqueous Fluorocopolymer Dispersion

Field of Technology

This invention relates to an aqueous fluorocopolymer dispersion that is of superior film forming capacity, transparency in clear coating and weathering resistance and that provides a coating film having a high gloss and superior mechanical properties. In greater detail, this invention relates to an aqueous fluorocopolymer dispersion prepared by seed polymerization of specified quantities of acrylic acid ester and/or methacrylic acid ester obtained by copolymerizing specified quantities of chlorotrifluoroethylene (CTFE) in vinylidene fluoride (VdF).

Background Technology

Fluorine paints are used as weather resistance materials for the outside trim and interior finish work of one to five story buildings. Various technologies have been developed for the purpose of obtaining these fluorine paints. Many fluorine paints are dispersed in organic solvents. However, the use of organic solvents presents problems in respect to safety and environmental protection, for which reason there is a desire for aqueous products. The following methods are known as methods for the manufacture of aqueous dispersions of fluorine polymers.

In Japanese Patent Announcement No. 4-55441 [1992] and Japanese Patent Application Early Disclosure No. 3-7784 [1991], it is indicated that film forming capacity and film transparency that cannot be obtained with emulsion blends can be obtained by emulsion polymerization of ethylenic unsaturated monomers in the presence of VdF copolymer particles. CTFE is one of the monomers that is copolymerized with VdF in the VdF copolymer. Examples of ethylenic unsaturated monomers include acrylic acid esters (EA) and methacrylic acid esters (MMA). However, the proportions of the combinations of VdF and CTFE and of the copolymers thereof are not specifically disclosed in these announcements. Moreover, seed polymerization of EA and MMA in th presence of copolymer particles of VdF and CTFE is not specifically disclosed. Further, there is no mention in these announcements of the gloss of the coating film, which is a property of practical importance for paints.

Although it is stated in these patent announcements that coating films of superior transparency and mechanical strength can be obtained, on the basis of the research of the inventors, the transparency of the coating films that are obtained does not reach a sufficient level for practical use as clear coatings. Thus, it was ascertained that further study is necessary

On the basis of research by the inventors, the compatibility of various types of VdF copolymers and acrylic resins is not sufficient for mixing of resins by seed polymerization, it is difficult to obtain transparent films at th time of film formation and high gloss paint films cannot be obtained.

In Japanese Patent Application Early Disclosure No. 1-190745 [1989], it is disclosed that organic solvent solutions of fluorocopolymers that have been polymerized in a nonaqueous system are converted to aqueous systems and vinyl monomers are polymerized in this aqueous system. It is indicated that the polymerization components of this fluorocopolymer are VdF and CTFE and that the vinyl monomers are EA and MMA. However, the proportions of the combinations of VdF and CTFE and of the copolymers are not specifically disclosed in this patent announcement and seed polymerization of EA and MMA in the presence of copolymer particles of VdF and CTFE is not specifically disclosed. Moreover, from the announcements, it can be seen that the films that are obtained are of inferior transparency and are do not display adequate mechanical properties.

In Japanese Patent Application Early Disclosure No. 4-189879 [1992], solution mixtures of VdF/TFE/CTFE ternary copolymers comprised of vinylidene fluoride, tetrafluoroethylene (TFE) and chlorotrifluoroethylene (CTFE) and acrylic resins are disclosed. Although mixing of VdF/TFE/CTFE ternary copolymers with acrylic resins is performed in the presence of an organic solvent, mixing in the presence of water is not discussed.

In Japanese Patent Announcement No. 57-14392 [1982], it is disclosed that a stable mixed emulsion can be obtained by adding a surfactant when VdF polymers and acrylic polymers are subjected to emulsion blending. However, with the technology disclosed in this announcement, blends at the molecular level are not formed as in the solvent type, transparent films cannot be obtained at the time of film formation and mechanical properties are not sufficient. Thus, the advantages of mixing cannot be obtained.

This invention was developed in the light of the problems described above and its objective is to obtain an aqueous fluorocopolymer dispersion which can provide coating films of superior film forming capacity, transparency in clear coating and weathering resistance, high gloss and superior mechanical properties.

The inventors arrived at this invention by discovering that blend aqueous dispersions at the molecular level can be obtained by seed polymerization of specified quantities of acrylic acid esters and/or methacrylic acid esters in the presence of fluorocopolymer particles (hereafter referred to as seed particles) in an aqueous dispersion containing fluorocopolymers of a limited composition containing 70 to 95% (mole %; the same hereafter) of VdF and 5 to 30% of CTFE in a VdF copolymer and that the aforementioned objectives can be achieved with this dispersion.

Disclosure of the Invention

Specifically, this invention relates to an aqueous fluorocopolymer dispersion that is prepared by seed polymerization of 20 to 100 parts of acrylic acid ester and/or methacrylic acid ester in the presence of 100 parts (parts by weight; the same hereafter) of fluorocopolymer particles in an aqueous dispersion that contains fluorocopolymer particles comprised of 70 to 95% of VdF and 5 to 30% of CTFE.

Optimum Mode for Execution of the Invention

The fluorocopolymer that is used as the seed particles in this invention should contain 70 to 95% of VdF and 5 to 30% of CTFE, preferably, 75 to 90% of VdF and 10 to 25% of CTFE, and, more preferably, 75 to 85% of VdF and 15 to 25% of CTFE.

When the VdF content is less than 70%, the compatibility of the seed particles with the acrylic and/or methacrylic copolymer is decreased and the superior characteristics attributable to compatibility such as the superior transparency and mechanical properties of the film that is formed when the emulsion is dried (hereafter called cast film) cannot be obtained. When the CTFE content is less than 5%, there is poor solubility of the seed crystals in the acrylic acid ester and/or methacrylic acid ester, for which reason swelling of the monomers to seed particles during seed polymerization does not proceed rapidly, the cast film from the emulsion that is obtained is of poor transparency and gloss cannot be obtained when a coating film is made from a paint.

The fluorocopolymer may contain a third copolymerizable monomer in addition to VdF and CTFE as a copolymerization component. The third copolymerizable monomer can be TFE, vinyl fluoride (VF), hexafluoropropylene (HFP) and trifluoroethylene (TrFE). TFE is preferable, but several different polymers may be used. The content of the third copolymerizable monomer should be 0 to 30%, preferably, 10 to 25%, and, more preferably, 10 to 20%.

When the seed particles do not contain CTFE and are comprised of VdF and TFE or VF, there is poor solubility of the seed particles in the monomer, swelling of the monomer to seed particles does not proceed rapidly during seed polymerization, the cast film from the emulsion that is obtained is of poor transparency and gloss cannot be obtained when a coating film is prepared fr m a paint.

When the seed particles do not contain CTFE and are comprised of VdF and HFP or TrFe, the seed particles exhibit solubility in the monomers depending on the copolymerization proportions. However, HFP and TrFE bring about a decrease in compatibility with acrylic and/or methacrylic copolymers, for which reason the cast film from the emulsion that is obtained is of poor transparency and a coating film of high gloss cannot be obtained.

The particle diameter of the seed particles is closely related to the particle diameter of the polymer particles after seed polymerization. In order to make the particle diameter of the polymer particles less than 250 nm after seed polymerization, it is desirable that it be less than 200 nm, preferably, less than 180 nm, and, more preferably, less than 150 nm.

The fluorocopolymers that are used as the seed particles can be obtained by the ordinary emulsion polymerization method. Aqueous emulsions containing seed particles of less than 200 nm in particle diameter can be prepared, for example, by emulsion polymerization of a monomer mixture containing VdF and CTFE in the presence of a fluorine surfactant in an amount relative to water of less than 1.0 wt %, preferably, less than 0.5 wt%, and, more preferably, less than 0.2 wt % (the lower limit ordinarily being 0.01 wt %) and of a nonionic nonfluorine surfactant in an amount relative to water of 0.001 to 0.1 wt %, and, preferably, 0.01 to 0.05 wt %. This aqueous dispersion can contain seed particles of less than 200 nm in particle diameter at high concentrations of 30 to 50 wt %. When the quantity of fluorine surfactant used is greater than 1.0 wt %, there are the undesirable tendencies of separating out of the surfactant onto the film, of increase in the water absorption rate or of turbidity in water when a film is formed from the aqueous dispersion. When the quantity of nonionic nonfluorine surfactant used is greater than 0.1 wt %, a decrease of the polymerization rate and cessation of the reaction occur due to chain transfer, which is not practical. At a weight % of less than 0.001 wt %, the effect of decreasing particle diameter is essentially not seen. Polymerization temperature should be 20 to 120°C, and, preferably, 30 to 70°C. When the polymerization temperature is less than 20°C, the stability of th latex that is produced is decreased. When the polymerization temperature is higher than 120°C, there is a tendency for stalling of the polymerization rate to occur due to chain transfer. Depending on the type of polym r, polymerization is ordinarily performed at a pressure of 1.0 to 50 kgf/cm2 (gauge pressure) by heating for 5 to 100 hours.

The fluorine surfactants that are used in emulsion polymerization of the seed particles are mixtures of 1 or 2 or more compounds that contain fluorine particles in their structures and that have surfactant capacity. For example, they include acids as indicated by $X(CF_2)_nCOOH$ (n indicating an integer of 6 to 20 and X indicating F or H) and alkali metal salts, ammonium salts, amine salts or quaternary ammonium salts thereof and acids as indicated by $Y(CH_2CF_2)_mCOOH$ (m indicating an integer of 6 to 13 and Y indicating F or Cl) and alkali metal salts, ammonium salts, amine salts or quaternary ammonium salts thereof. More specifically, ammonium salts of perfluorooctanoic acid and ammonium salts of perfluorononanoic acid can be used. In addition, known fluorosurfactants can also be used.

The nonionic nonfluorine surfactants that are used in emulsion polymerization of seed particles include polyoxyethylene alkyl ethers, polyoxyethylene alkylphenyl ethers, polyoxyethylene alkyl esters, sorbitan alkyl esters; polyoxyethylene sorbitan alkyl esters, glycerol esters and derivatives thereof. More specifically, the polyoxyethylene alkyl ethers can include polyoxyethylene lauryl ether, polyoxyethylene cetyl ether, polyoxyethylene stearyl ether, polyoxyethylene oleyl ether and polyoxyethylene behenyl ether; the polyoxyethylene alkylphenyl ethers can include polyoxyethylene nonylphenyl ether and polyoxyethylene octylphenyl ether, the polyoxyethylene alkyl esters can include monolauric acid polyethylene glycol, monooleic acid polyethylene glycol and monostearic acid polyethylene glycol, the sorbitan alkyl esters can include monolauric acid polyoxyethylene sorbitan, monopalmitic acid polyoxyethylene sorbitan, monostearic acid polyoxyethylene sorbitan and monooleic acid polyoxyethylene sorbitan; the polyoxyethylene sorbitan alkyl esters can include monolauric acid polyoxyethylene sorbitan, monopalmitic acid polyoxyethylene sorbitan and monostearic acid polyoxyethylene sorbitan and the glycerol esters can include monomyristic acid glyceryl, monostearic acid glyceryl and monooleic acid glyceryl. Derivatives thereof can include polyoxyethylene alkylamines, polyoxyethylene alkylphenyl - formaldehyde condensates and polyoxyethylene alkyl ether phosphates. Polyoxyethylene alkyl ethers and polyoxyethylene alkyl esters having HLB values of 10 to 18 are particularly desirable. Specifically, polyoxyethylene lauryl ether (EO : 5 to 20; EO indicating the number of ethylene oxide units), monostearic acid polyethylene glycol (EO: 10 to 55) and monooleic acid polyethylene glycol (EO: 6 to 10) can be cited.

In this invention, monomers that contain acrylic acid esters and/or methacrylic acid esters are seed polymerized in the presence of seed particles. There are cases in which the monomer is comprised only of acrylic acid esters and/or methacrylic acid esters and there are cases in which they are used in combination with copolymerizable monomers.

From the standpoint of compatibility with fluorocopolymers, ethyl acrylate is preferable as the acrylic acid ester and methyl methacrylate and ethyl methacrylate are preferable as the methacrylic acid ester. One or two or more of these may be used in combination.

Monomers other than acrylic acid esters and methacrylic acid esters that can be copolymerized with them can be seed polymerized with the acrylic acid esters and/or methacrylic acid esters. Ethylenic unsaturated monomers are preferable as copolymerizable monomers.

Ethylenic unsaturated monomers include monomers having functional groups and vinyl compounds. Monomers having functional groups include, for example, unsaturated carboxylic acids such as acrylic acid (AAc), methacrylic acid, maleic acid and crotonic acid, amide compounds such as acrylamide, methacrylamide, N-methylolacrylamide, N-butoxymethylacrylamide, N-methylolmethacrylamide, N-methylmethacrylamide and N-butoxymethylmethacrylamide, monomers containing hydroxyl groups such as hydroxyethyl acrylate, hydroxyethyl methacrylate (HEMA), hydroxypropyl acrylate and hydroxypropyl methacrylate, monomers containing epoxy groups such as glycidyl acrylate and glycidyl methacrylate, monomers containing silanol

groups such as γ-trimethoxysilane methacrylate and γ-triethoxysilane methacrylate and monomers containing aldehydes such as acrolein. The vinyl compounds include, for example, styrene (St) and acrylonitrile.

When the aforementioned ethylenic unsaturated monomers are used in combination, the quantity of acrylic acid ester and/or methacrylic acid ester should be greater than 60 wt %, preferably, 70 to 100 wt %, and, more preferably, 80 to 100 wt % relative to the total quantity of the monomer mixture. When it is less than 60 wt %, it exhibits poor compatibility with the seed particles and there is a tendency for the transparency of the formed film and the gloss of the coating film, which are the objectives of this invention, to be decreased.

The total quantity of the aforementioned ethylenic unsaturated monomers and acrylic acid esters and/or methacrylic acid esters that is used should be 20 to 100 parts, preferably, 30 to 100 parts, and, more preferably, 40 to 100 parts, per 100 parts of seed particles. When it is less than 20 parts, there is a tendency for transparency and for gloss on film coating to be decreased.

Seed polymerization of acrylic acid esters and/or methacrylic acid esters and ethylenic unsaturated monomers can be performed under the same conditions as for ordinary emulsion polymerization. For example, a surfactant, a polymerization initiator, a chain transfer agent, and, as required, a chelating agent, a pH regulator and a solvent, are added to an aqueous medium containing the seed particles and a reaction is carried out for 0.5 to 6 h urs at a temperature of 20 to 90°C, preferably, 20 to 80°C, and, more preferably, 30 to 70°C.

In seed polymerization, a method in which the total quantity of monomer is introduced all together into the reaction system in the presence of the seed particles, a method in which some of the monomer is introduced and reacted, after which the remainder is introduced continuously or in batches r a method in which the total quantity of monomer is introduced continuously may be used.

When acrylic acid esters, methacrylic acid esters and ethylenic unsaturated monomers are seed polymerized by the emulsion polymerization method in the presence of seed particles, swelling to the seed crystals first occurs. At this time, the seed crystals are in the state of an aqueous dispersion that is uniformly dissolved in the monomer, the monomer is polymerized by addition of a polymerization initiator and mixed particles that entwined around the molecular chain are formed. An interpenetrating network structure (IPN) can also be formed by copolymerization of a polyfunctional monomer. These polyfunctional monomers include monoglycol dimethacrylate and diglycol dimethacrylate.

The surfactants that can be used include anionic surfactants and nonionic surfactants, which can be used in combination. Amphoteric surfactants can also be used. The anionic surfactants that can be used include esters of higher alcohol sulfates such as, for example, sodium salts of alkyl sulfonic acids, sodium salts of alkyl benzenesulfonic acids, sodium salts of succinic acid dialkyl ester sulfonic acids and sodium salts of alkyl diphenyl ether disulfonic acids. The nonionic surfactants that can be used include polyoxyethylene alkyl ethers, polyoxyethylene alkylphenyl ethers, polyoxyethylene alkyl esters, polyoxyethylene alkylphenyl esters, sorbitan alkyl esters, glycerol esters and derivatives thereof. An amphoteric surfactant that can be used is lauryl betaine. Emulsifying agents that are copolymerizable or reactive with acrylic acid esters, methacrylic acid esters and ethylenic unsaturated monomers, for example, sodium styrene sulfonate and sodium alkyl sulfosuccinate, can be used. The quantity of surfactant that is used should be on the order of 0.05 to 5.0 parts per total of 100 parts of methacrylic acid ester and ethylenic unsaturated monomer.

There are no particular limitations on the polymerization initiators as long as they produce radicals that can be used in free radical reactions in aqueous media between 20 to 90°C. Depending on the circumstances, they can be used in combination with a reducing agent. Ordinarily, persulfates and hydrogen peroxide can be used as water-soluble polymerization initiators and sodium pyrobisulfite, sodium hydrogensulfite and sodium L-ascorbate. Oil-soluble polymerization initiators include diisopropyl peroxy carbonate (IPP), benzoyl peroxide, dibutyl peroxide and azobisisobutyronitrile (AIBN). The quantity of polymerization initiator used is ordinarily on the order of 0.05 to 2.0 parts per total of 100 parts of acrylic acid ester, methacrylic acid ester and ethylenic unsaturated monomer.

The polymerization temperature should be in the range of 20 to 90°C, and, preferably, 30 to 70°C.

The chain transfer agents that can be used include halogenated hydrocarbons (for example, chloroform and carbon tetrachloride) and mercaptans (for example, n-dodecylmercaptan, t-dodecylmercaptan and n-octylmercaptan). The quantity of chain transfer agent is ordinarily on the order of 0 to 5.0 parts per total of 100 parts of acrylic acid ester, methacrylic acid ester and ethylenic unsaturated monomer.

The solvents that can be used include small quantities of methyl ethyl ketone, acetone, trichlorotrifluoroethane, methyl isobutyl ketone and acetic acid esters in ranges that do not impair workability, disaster prevention safety, environmental safety and manufacturing safety. Monomer swelling capacity to the seed crystals is improved by adding a solvent.

The aqueous fluorocopolymer dispersion of this invention is obtained as described above. From the standpoint of improving film forming capacity, which is an objective of this invention, it is desirable to perform the seed polymerization of methacrylic acid esters and monomers that are copolymerizable with them in the presence of an aqueous dispersing element containing fluorocopolymer particles having a Tg ranging from -35°C to 25°C. By this means, the minimum film forming temperature of the aqueous fluorocopolymer dispersion can be set as desired in a range of 0°C to 70°C by selecting the Tg of the seed particles as described above.

Setting of the Tg of the fluorocopolymer in the aqueous dispersing element can be controlled by a known method, i.e., on the basis of the copolymerization proportion of vinylidene fluoride with other fluorine monomers. In respect to Tg, a Tg formation rule for homopolymers has generally been established for compatible resin systems of copolymerization systems. In order to set the Tg of a resin of an aqueous fluorocopolymer dispersion to on the order of 0 to 70°C, it is desirable that the Tg of the fluorine copolymer be -35 to 25°C. It is desirable that the monomer that is seed polymerized be a methacrylic acid ester having 1 to 6 carbon atoms in the side chain that contains more than 80 wt % of monomer that is added during seed polymerization.

Methacrylic acid esters having 1 to 6 carbon atoms in the side chain are desirable because they have little effect on decrease of weathering resistance. However, because compatibility with VdF copolymer resins increases as the number of carbon atoms in the side chain decreases, methacrylic acid esters having 1 to 3 carbon atoms in the side chain are preferable and methyl methacrylate having 1 carbon atom in the side chain is even more preferable.

Monomers that are copolymerizable with the aforementioned methacrylic acid esters are (I) monomers having reactive functional groups, f r example, unsaturated carboxylic acid such as acrylic acid, methacrylic acid, maleic acid and crotonic acid, amide compounds such as acrylamide, methacrylamide, N-methylacrylamide, N-methylolacrylamide, N-butoxymethylacrylamide,

N-methylolmethacrylamide, N-methylnethacrylamide and N-butoxymethylmethacrylamide, monomers containing hydroxyl groups such as hydroxyethyl acrylate, hydroxyethyl methacrylate, hydroxypropyl acrylate and hydroxypropyl methacrylate, monomers containing epoxy groups such as diglyceryl acrylate and diglyceryl methacrylate, monomers containing silanol groups such as γ-trimethoxysilane methacrylate and γ-triethoxysilane methacrylate and monomers containing aldehydes such as acrolein, and, (II) as other vinyl compounds, styrene and acrylonitrile.

In addition, polyfunctional monomers such as ethylene glycol dimethacrylate and propylene glycol dimethacrylate can be copolymerized for the purpose of improving resistance to solvents and water resistance.

Further, when emulsion polymerization is performed in the presence of these aqueous dispersing element particles, compounds containing polymers or oligomers of low molecular weights containing hydrophilic sites can also be used as monomers having copolymerizable ethylenic unsaturated bonds. The aforementioned term hydrophilic site indicates sites having hydrophilic groups or sites having hydrophilic bonds and sites in which they are combined. These hydrophilic groups may be anionic, nonionic and amphoteric groups and combinations thereof. However, nonionic and anionic hydrophilic groups are preferable. They may also contain known reactive emulsifying agents.

Examples of the aforementioned monomers and reactive emulsifying agents included marketed substances such as Burenma [phonetic]* PE-350, Burenma PME-400 and Burenma 70PEP350B (manufactured by Nippon Oils and Fats (Ltd.)), NK Ester M-40G, NK Ester M-90G, NK Ester M-230G, NK Ester AMP-60G, NK Ester CB-1, NK Ester SA and NK Ester A-SA (manufactured by Shin Nakamura Kagaku (Ltd.)) and Eleminol [phonetic] JS2 and Eleminol R360 (Manufactured by Sanyo Kasei Kogyo (Ltd.)).

Of the aforementioned monomers, methacrylic acid ester derivatives, which do not have deleterious effects on weathering resistance, are preferable.

The average particle diameter of the polymer particles of the aqueous dispersion that is obtained by seed polymerization in this invention should be 50 to 250 nm, preferably, 100 to 200 nm, and, in particular, 100 to 160 nm. When the average particle diameter is less than 50 nm, the viscosity of the aqueous dispersion is increased and a high concentration aqueous dispersion cannot be obtained. When the average particle diameter of the polymer particles exceeds 250 nm, precipitation and solidification of the particles occur when the aqueous dispersion is stored. In addition, there is the problem that gloss does not appear at the time the coating film is prepared.

The aqueous fluorocopolymer dispersion of this invention and can also be used as a protective surface coating for concrete or as a coating material f r coated paper by compounding additives that are generally used in aqueous emulsion type paints such as pigments, thickeners, dispersing agents, defoaming agent, antifreezing agents and auxiliary film forming agents.

Next, we shall describe this invention by presenting examples. However, this invention is not limited to these examples.

Example of Manufacture 1

500 ml of deionized water, 0.5 g of ammonium salt of perfluorooctanoic acid and 0.05 g of polyoxyethylene monostearic acid ester (MYS25, manufactured by Nikko Chemicals), which is a nonionic nonfluorine surfactant, were introduced into a pressure-resistant reactor of an internal capacity of 1 liter equipped with a stirrer, nitrogen was introduced under pressure, deaeration was repeated and the dissolved air was removed, after which a VdF/CTFE fluorine monomer mixture at a molar rati of 93/7 was supplied continuously and a reaction was carried out for 30 hours. Following that, the

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*Translator's Note: Transliterated phonetically from the Japanese. As such, the spelling may differ from other transliterations.

interior of the tank was restored to normal temperature and normal pressure and the reaction was considered to have been completed. Determinations were made of the following items for the seed crystals, which were comprised of VdF/CTFE, and for the aqueous dispersion containing the seed crystals. The results are shown in Tabl 1.

Concentration of solid components: The materials were dried for 1 hour in a vacuum dryer at 150°C and the weight after drying is expressed by a percentage relative to the weight of the aqueous dispersion before drying.

Average particle diameter: The determinations were made with a laser light scattering particle diameter determination apparatus (ELS-3000, manufactured by Otsuka Denshi (ltd.)).

Intrinsic viscosity: Intrinsic viscosity [η] at 35°C was determined as an MEK solution.

Examples of Manufacture 2 through 15

Aqueous dispersions 2 through 15 containing seed particles were manufactured in the same way as in Example 1 except that the compositions (mole %) of the fluorine monomers were varied as shown in Table 1. The concentration of the solid components were determined in the same way as in Example of Manufacture 1. The results are shown in Table 1.

[blank below]

Table 1

		89/11 Examples of Manufacture														
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
	VdF	93	80	88	80	74	70	97	90	67	60	68	74	83	82	83
	CTFE	7	20	6	5	14	10	3		33	15					
	TFE			6	15	12	20		10		15	32	18			
	HFP												8	17		
	VF														18	
	TrFE	58 ~~<60~~	<60	<60		≮60	62	<60	≮60	<60	>64	≥69	^	≥64	<60	17 <62
A	平均粒径 (nm)	126.3	141.2	134.1	143.5	138.0	136.0	131.0	123.2	133.5	141.3	151.6	135.0	143.6	121.4	156.0
B	極限粘度 [η]	1.85	1.68	1.75	1.78	1.48	1.37	1.81	B1	1.56	1.73	B1	1.55	1.58	B1	1.65
C	固形分濃度 (重量%)	27.1	34.3	28.2	33.6	35.0	32.8	24.3	21.0	34.5	32.6	23.7	35.1	34.2	20.8	22.3

HFP

Key to translation of Table 1:
A = Average particle diameter (nm)
B = Intrinsic viscosity [η]
C = Concentration of s lid components (wt %)

B1 = insoluble

Example 1

Experimental Example 1

70 g of the aqueous dispersion obtained in Example of Manufacture 1 was introduced into a four-neck flask of an internal capacity of 200 ml equipped with a stirring blade, a condenser tube and a thermometer and sodium dodecyl benzenesulfonate and Triton X100 (manufactured by the Union Carbide Company) as a nonionic surfactant were added in amounts of 0.5 wt % relative to the solid components. The mixture was heated in a water bath as it was being stirred. When the tank temperature reached 80°C, an emulsion comprised of the solid component and an equal quantity of a monomer mixture of methyl methacrylate (hereafter referred to MMA) and ethyl acrylate (hereafter referred to EA) in a weight ratio of 50/50 emulsified in an 0.5 wt % aqueous solution of MYS25 (manufactured by Nikko Chemicals (Ltd.)) was added dropwise over a one hour period. Immediately thereafter, 1 ml of a 2 wt % aqueous solution of ammonium persulfate was added and a reaction was initiated. Three hours after the reaction was begun, the temperature in the tank was raised t 85°C and this temperature was maintained for one hour, after which it was cooled. The pH was then adjusted to 7 with the ammonia water, after which filtering was performed with 300 mesh wire netting, with a bluish-white aqueous fluorocopolymer dispersion being obtained.

The items indicated below were determined for this aqueous dispersion.

(1) Evaluation of the characteristics of the aqueous dispersing element

Concentration of the solid component and average particle diameter: Same methods as in Method of Manufacture 1.

Minimum film forming temperature (MFT): The minimum temperature at which continuous film formation occurred with a heat gradient testing apparatus (manufactured by Rigaku Kogyo (Ltd.)). Film formation is possible at lower temperatures as MFT decreases.

(2) Evaluation of the characteristics of the formed film

Transparency: The aqueous dispersion was poured into a laboratory dish of 10 cm in diameter so that the thickness of the dried film was 200 μm and the materials were dried for 24 hours at 50°C. However, in Experimental Example 25, drying was carried out for 24 hours at 80°C. Light ray permeability of these film was determined at a wavelength of 800 nm and evaluations were made as follows.

O: Transparent (permeability exceeding 90%)

Δ: Semitransparent (permeabilities of 60 to 90%)

X: Turbid (permeability of less than 60%)

(3) Evaluation of characteristics of the coating film

50 parts of titanium oxide (Product name, CR90 (manufactured by Ishihara Sangyo (Ltd.)) as a filler, 2 parts of Discote [phonetic] H-14 (manufactured by Nippon Nyukazai (Ltd.)) as the dispersing agent, 1 part of ethylene glycol as the antifreezing agent, 0.5 parts of FS Antifoam 013B (manufactured by Nippon Nyukazai (Ltd.)) as the defoaming agent, 0.5 parts of SN Thickener A-818 (manufactured by Sannopuko [phonetic] (Ltd.)) as the thickener and 10 parts of Dexanol [phonetic] CS12 (manufactured by Chisso (Ltd.)) as the auxiliary film forming agent were added to 100 parts of the s lid components of the aqueous dispersion obtained in Experimental Example 1 and these substances were thoroughly mixed using a Dispa [phonetic] stirrer, with a paint being prepared.

Gloss: The paint that was obtained was extended on a glass plate using an applicator so that the thickness of the coating film was 20 μm and the materials were dried for one week at room temperature, after which gloss was determined (determination angle, 60°) using a gloss meter (manufactured by Suga Shikkenki (Ltd.)).

Weathering resistance: The paint that was obtained was applied with an airless spray gun to a slate plate that had been subjected to primer treatment with DAN White Sealer (manufactured by Nippon Paint (Ltd.)) so that the coating thickness after drying was 100 μm. The slate plate to which it had been applied was dried for 24 hours at room temperature, after which it was dried for 2 hours at 80°C. The gloss retention ratio of the coated plate after 1000 hours in an accelerated weathering resistance testing device (SUV) was determined and evaluations were made as indicated below.

O: Gloss retention ratio exceeding 80%

Δ: Gloss retention ratio of 60 to 80%

X: Gloss retention ratio of less than 60%

Resistance to alkalies: A coated plate prepared in the same way as for the weathering resistance test was immersed for one week at 50°C in a 3 wt % aqueous solution of NaOH, after which coloration and swelling of the coating film were evaluated visually.

Resistance to acids: A coated plate prepared in the same way as for the weathering resistance test was immersed for one week at 50°C in a 1 wt % aqueous solution of sulfuric acid, after which coloration and swelling of the coating film were evaluated visually.

Examples 2 through 15

Seed polymerization was performed by the same method as in Experimental Example 1 using the aqueous dispersions obtained in Examples of Manufacture 2 through 15 and the same tests were performed. The results are shown in Table 2.

[blank below]

Table 2

		Experimental Examples														
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
A	シード粒子／単量体の重量比	50/50	50/50	50/50	50/50	50/50	50/50	50/50	50/50	50/50	50/50	50/50	50/50	50/50	50/50	50/50
	MMA	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50
	EA	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50
B	固形分濃度（重量%）	37.4	47.3	37.6	46.1	47.6	45.0	33.3	28.5	47.6	44.7	32.7	48.2	46.7	28.7	30.1
C	平均粒径（nm）	186.4	198.1	197.6	210.0	204.1	197.6	193.3	183.9	194.5	208.3	214.1	199.5	212.0	187.3	230.1
D	最低成膜温度（℃）	32	8	21	15	8	13	39	47	9	13	26	12	11	19	42
E	クラック	E1	E1	E1	E1	E1	E1	E2	E3	E1	E1	E2	E1	E1	E3	E3
F	透明性	○	○	○	○	○	○	△	×	△	△	×	△	△	×	×
G	破壊強さ（kgf/cm^2）	280	58	234	275	160	203	-	-	53	73	-	82	69	-	-
H	破壊伸び（%）	290	460	285	212	360	312	-	-	430	347	-	210	251	-	-
I	耐候性	○	○	○	○	○	○	-	-	○	○	-	○	○	-	-
J	耐アルカリ	○	○	○	○	○	○	-	-	○	○	-	○	○	-	-
K	耐酸性	○	○	○	○	○	○	-	-	○	○	-	○	○	-	-
L	光沢（60° G）	58.5	59.7	64.2	73.6	76.0	74.2	-	-	41.3	39.5	-	46.2	43.1	-	-

TFE ~~HFP~~ TFE HFP

Key to translation of Table 2
A = Seed particles/monomer weight ratio
B = Concentration of solid components (wt %)
C = Average particle diameter (nm)
D = Minimum film forming temperature (°C)
E = Cracks E1 = None E2 = A few E3 = Present
F = Transparency
G = Breaking strength (kgf/cm^2)
H = Breaking el ngati n (%)
I = Weathering resistance;
J = Resistance to alkalies
K = Resistance to acids
L = Gl ss (60° G); [58.5]

From Table 2, it can be seen that the transparency of the formed film decreased and that the coating film did not exhibit gloss when there was less than 70% of VdF units. Even when there were more than 70% of VdF units, there was no film forming capacity of the formed film exhibited decreased transparency and the coating film did not exhibit gloss when there was less than 5% of the CTFE component in the copolymerization monomers or when a copolymerization monomer other than CTFE was used.

Example 2

Experimental Examples 16 through 25

Seed polymerization was performed and evaluations were made in the same way as in Experimental Example 1 using the aqueous dispersion obtained in Example of Manufacture 5 (the Tg of the seed particles being 16°C) and using MMA, EA, butyl acrylate (BA), acrylic acid (AAc), hydroxyethyl methacrylate (HEMA), styrene (St) and cyclohexyl methacrylate (CHMA) in the quantities shown in Table 3. The results are shown in Table 3.

[blank below]

Table 3

F/.

		Experimental Examples									
		16	17	18	19	20	21	22	23	24	25
A	シード粒子/単量体の重量比	70/30	50/50	50/50	50/50	50/50	50/50	50/50	50/50	50/50	50/50
	MMA	100		50	50	40	60				100
	EA		100	45	45	30		50		50	
	BA						40		100		
	AAc			5							
	HEMA				5						
	St					30		50			
	CHMA	40								50	
B	固形分濃度（重量%）	39.4	45.2	45.5	46.3	43.6	45.0	44.9	46.1	47.1	46.3
C	平均粒径 (nm)	157.8	182.0	175.2	178.3	175.4	173.5	175.1	181.6	183.3	178.1
D	最低成膜温度（℃）	42	7	15	15	28	17	39	18	—	69
E	クラック	E1	E1	E1	E1	E1	E1	E1	E1	E2	E1
F	透明性	○	○	○	○	○	○	△	△	×	○
G	破壊強さ (kgf/cm^2)	2.62	0.51	1.50	1.83	2.81	2.00	1.31	0.20	0.37	3.58
H	破壊伸び（%）	244	473	367	330	281	245	321	420	285	108
I	耐候性	○	○	○	○	○	○	○	○	—	○
J	光沢	69.0	72.5	75.4	73.2	61.3	74.8	56.3	62.0	—	71.3

Key to translation of Table 3:
A = Seed particles/monomer weight ratio
B = Concentration of solid components (wt %)
C = Average particle diameter (nm)
D = Minimum film forming temperature (°C)
E = Cracks E1 = None E2 = A few
F = Transparency
G = Breaking strength (kgf/cm^2)
H = Breaking elongati n (%)
I = Weathering resistance;
J = Gloss

Possibility of industrial use

By means of the aqueous fluorocopolymer dispersion of this invention, coating films of superior film forming capacity, transparency on clear coating and weathering resistance, of high gloss and of superior mechanical properties can be provided.

Claims

1. An aqueous fluorocopolymer dispersion that is obtained by seed polymerization of 20 to 100 parts by weight of acrylic acid ester and/or methacrylic acid in an aqueous dispersion containing fluorocopolymer particles comprised of 70 to 95 mole % of vinylidene fluoride and 5 to 30 mole % of chlorotrifluoroethylene in the presence of 100 parts by weight of said fluorocopolymer particles.

2. An aqueous fluorocopolymer dispersion that is obtained by seed polymerization of 20 to 100 parts by weight of a monomer mixture of acrylic acid ester and/or methacrylic acid and a monomer that can be copolymerized with them in an aqueous dispersion containing fluorocopolymer particles comprised of 70 to 95 mole % of vinylidene fluoride and 5 to 30 mole % of chlorotrifluoroethylene in the presence of 100 parts by weight of said fluorocopolymer particles.

3. An aqueous fluorocopolymer dispersion as described in Claim 2 in which the aforementioned monomer mixture contains 60 to 100 parts by weight of acrylic acid ester and/or methacrylic acid ester.

4. An aqueous fluorocopolymer dispersion as described in Claims 1, 2 r 3 in which the acrylic acid ester and/or methacrylic acid ester is at least one substance selected from a group comprised of ethyl acrylate, methyl methacrylate and ethyl methacrylate.

In the seeds $VF_2/CTFE$

95/5 mol% → 91/9 w% F% = 58.6

70/30 " → 56/44 = 57.7

in the film F%

%F for 20% Acrylics 48.8

29.3

%F for 100% Acrylics 29.3

28.8

In example # 11, 12, 13 F% ≯ 33 & no. cl → not clear fil

It is said in the text also, p.4